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Ionic Strength Dependence of Ion Adsorption at the Rutile/Aqueous Interface Using X-ray Standing Wave Method

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Beamline(s): X15A

Introduction: The electrical double layer (EDL) is very important to understand many natural and industrial processes, e.g., water purification and catalysis. Since the EDL concept was introduced more than a century ago, numerous efforts have been carried out to describe the EDL structure. Gouy-Chapman-Stern model is an well-accepted model that predicts that ions near a charged interface form a condensed layer at the interface followed by a diffuse layer extended into the bulk solution. Many aspects of the model have not been well tested because of lack of direct experimental results of the EDL structure. High brilliance X-ray sources offer powerful approaches to probe the EDL structure, e.g. X-ray Standing Waves (XSW) and X-ray surface diffraction. Rutile (TiO_2) is one of the most studied oxide surfaces [1], and represents an important model system for understanding the EDL structure. Extensive surface charging measurements have been carried out at the rutile/aqueous interface [2]. In our earlier work [3], we studied the adsorption of Sr^{2+} and Rb^{+} at the aqueous/TiO_2 (110) interface with XSW and EXAFS. Our present work is focused on the ionic strength dependence of the adsorbed ion position at the interface.

Methods and Materials: The TiO_2 single crystal ($10\times10\times1mm^3$) was hydrothermally treated and cleaned to remove any pre-absorbed impurities. The crystal was then sealed into a specially designed cell with a thin kapton film. Solutions were injected into the cell for each measurement. The XSW measurements were performed with solution having [Sr^{2+}]=0.1mM at pH=10.7, and the ionic strength was controlled by NaCl concentration. The RbOH solutions with the Rb^{+} concentration ranging from 0.1mM to 1mM were also measured.

The measurements were performed at beamline X15A at National Synchrotron Light Source. A 6° miscut Si (111) monochromator was used to select the x-ray energy at 17keV. The single crystal TiO_2 (110) reflection was measured. The fluorescence detector collected the fluorescence signal from the crystal surface at a take-off angle less than 5°. The coverage of the Sr^{2+} and Rb^{+} ions on the surface was calibrated with a Sr^{2+} implanted standard. We measured a surface coverage of about ca. 0.25 monolayer (ML).

Results: The experimentally measured (110) reflectivity, R(θ), and Sr^{2+} XSW fluorescence yield, Y(θ), are presented in Fig.1, along with the best-fit curves to the data. The corresponding coherent fractions and the coherent positions of Sr^{2+} are shown in the figure. The Sr^{2+} coherent positions are the same for different ionic strength, which implies that the Sr^{2+} ions locate in the condensed layer dominantly, and the condensed layer position is independent of the ionic strength of the solution.

The XSW measurements of Rb^{+} show that there is no significant ordering of Rb ions at the TiO_2 surface in the range of [Rb^{+}] we measured. This means that there is no condensed layer formed at the interface under these conditions. One of the measurements is shown in Fig. 2.

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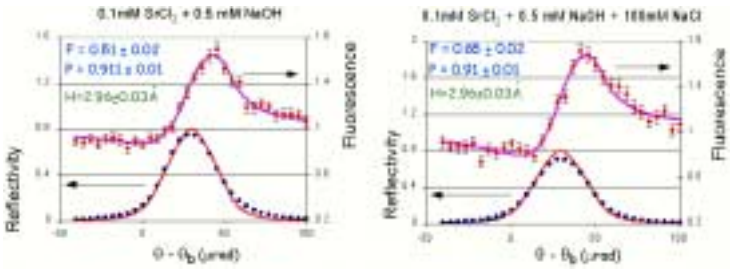

Figure 1. XSW results for Sr^{2+} absorbed on TiO_2 (110) surface.

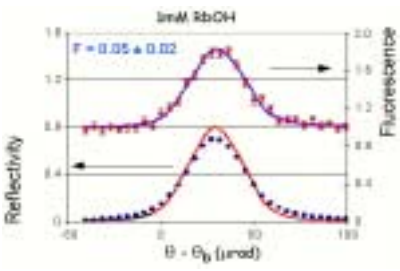

Figure 2. XSW results for Rb^{2+} absorbed on TiO_2 (110) surface.